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TITLE: Conformal thin films over textured capacitor electrodes

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Brief Summary Text - BSTX (26):

Similar alternating chemistries are preferably employed to form top electrode materials over the conformal dielectric layers. Examples are provided herein for metal nitride **barriers** as well as elemental metal layers. Following formation of thin, conformal conductive layer(s) by the preferred methods, conventional deposition with reduced conformability can complete the desired thickness of the top electrode without sacrificing capacitance. Conformal capacitor dielectric and top electrodes formed by the preferred methods thus enable taking full advantage of the increased surface area afforded by textured bottom electrodes.

Drawing Description Text - DRTX (12):

FIG. 8 is a partial, schematic cross-section of a partially fabricated memory cell capacitor, including a conformal ultrathin dielectric over a **barrier** layer and HSG silicon;

Drawing Description Text - DRTX (14):

FIG. 10 is a partial, schematic cross-section of a memory cell capacitor with an HSG silicon bottom electrode, including both a conformal ultrathin dielectric and a conformal **barrier** layer thereover.

Detailed Description Text - DETX (24):

Desirably, the reaction 108 is also self-limiting. Reactants saturate the limited number of reaction sites left by step 104. Temperature and pressure conditions are preferably arranged to avoid diffusion of reactants from the second chemistry through the monolayer to underlying materials. The second chemistry also leaves a surface termination that is not reactive with excess reactants in the second chemistry, thus operating to limit the deposition in a saturative reaction phase. In the illustrated embodiments of Tables I to V below, hydroxyl (OH) tails and oxygen **bridge** termination on a metal oxide monolayer are non-reactive with excess oxygen source gases of the second chemistry.

Detailed Description Text - DETX (45):

During the oxygen pulse 108, the oxygen source gas reacts with or chemisorbs upon the self-terminated metal complex monolayer left by the first phase 107. In the illustrated embodiments, this chemisorption comprises a saturative ligand-exchange reaction, replacing the organic ligand or halide termination of the metal-containing monolayer with oxygen or an oxygen complex. Metal oxide is thereby formed, preferably in a single monolayer. Desirably, the process leaves a stoichiometric metal oxide, with hydroxyl and oxygen **bridge** termination. As discussed with respect to the metal phase 107, the monolayer need not occupy all available sites, due the physical size of the adsorbed complex. However, the second phase 111 also has a self-limiting effect.

Detailed Description Text - DETX (46):

In particular, the oxygen source gas reacts with the ligand of the metal complex chemisorbed onto the workpiece surface during the previous pulse of metal source gas. The reaction is also surface limiting or terminating, since the oxidant during the pulse 108 will not react with the hydroxyl and oxygen **bridge** termination of the metal oxide monolayer. Moreover, temperature and pressure conditions are arranged to avoid diffusion of the oxidant through the metal monolayer to underlying materials. Despite longer exposure to a greater concentration of reactants in this saturative, self-limiting reaction phase 111, the thickness of the metal oxide formed on upper surfaces of the HSG silicon grains does not exceed the thickness of the metal oxide formed in the neck regions between grains.

Detailed Description Text - DETX (58):

Table II above presents parameters for ALD of a tantalum oxide (Ta.sub.2 O.sub.5) over HSG silicon of a capacitor bottom electrode. Preferably, the illustrated dielectric deposition is preceded by formation of a **barrier** layer to protect the HSG silicon from oxidation. In the illustrated embodiment, a dielectric **barrier** is formed, specifically comprising silicon nitride (Si.sub.3 N.sub.4). Advantageously, silicon nitride can be formed over HSG silicon with near perfect conformality by thermally nitriding the silicon surfaces. In other arrangements, a thin oxide layer can be first grown (e.g., by thermal oxidation) over the HSG silicon, followed by thermal nitridation of the oxide surface, as is known in the art.

Detailed Description Text - DETX (59):

Following formation of the **barrier** layer, Ta.sub.2 O.sub.5 is formed in an ALD process. As indicated in Table II, the illustrated metal source gas comprises tantalum ethoxide (Ta(OCH.sub.2 CH.sub.3).sub.5); the carrier gas

comprises nitrogen (N.sub.2); and the oxygen source gas preferably comprises ozone (O.sub.3). The temperature during the process is preferably kept between about 150.degree. C. and 300.degree. C., and more preferably at about 220.degree. C.

Detailed Description Text - DETX (65):

Table III above presents parameters for another ALD process for depositing tantalum oxide (Ta.sub.2 O.sub.5) over HSG silicon of a capacitor bottom electrode. Following formation of the silicon nitride **barrier** layer, as described above, Ta.sub.2 O.sub.5 is formed in an ALD process. As indicated in Table III, the preferred metal source gas comprises tantalum chloride (TaCl.sub.5); the carrier gas again comprises nitrogen (N.sub.2); and the oxygen source gas preferably comprises water vapor (H.sub.2 O). Temperatures during the process are preferably between about 150.degree. C. and 300.degree. C., and more preferably about 300.degree. C.

Detailed Description Text - DETX (85):

During the metal phase, a zirconium-containing monolayer is self-terminated with chloride tails. The termination of this monolayer does not readily react with ZrCl.sub.4 under the preferred conditions. In the next phase, water vapor oxidizes the metal containing monolayer, replacing chloride termination with hydroxyl and oxygen bridge termination. Then the preferred silicon source gas reacts with or adsorbs upon the hydroxyl and oxygen **bridge** termination during the silicon phase in a ligand-exchange reaction limited by the supply of metal oxide complexes previously adsorbed. Moreover, the preferred silicon source gas leaves an organic (ethoxide) or halide (chloride) termination that does not further react with excess silicon ethoxide in the saturative phase. Finally, ozone oxidizes the previously adsorbed silicon-containing monolayer to leave a ternary oxide.

Detailed Description Text - DETX (96):

The initial conductive thin film(s) can comprise any suitable conductive material, including silicon, metal nitrides and elemental metals, composites thereof and nanolaminates thereof Depending upon the material of the dielectric capacitor, a **barrier** layer may be desired over the dielectric. Particularly when employing Ta.sup.2 O.sub.5, a **barrier** thereover prevents oxidation of the remainder of the top electrode. The remainder of the top electrode can then be completed by conventional deposition of a conductive film, such as silicon or metal.

Detailed Description Text - DETX (97):

In the example of Table VII below, the top electrode comprises a conductive

metal nitride, which can serve as a **barrier** layer over Ta.sub.2 O.sub.5, deposited by an ALD process to conformally and continuously coat the capacitor dielectric. The example of Table VIII below the top electrode comprises an elemental metal layer, which can overlie or replace the **barrier** of Table VII, also formed by an ALD process.

Detailed Description Text - DETX (98):

Table VII above presents parameters for ALD of a conformal metal nitride **barrier** over a capacitor dielectric. The process is similar to that of FIGS. 4A and 5, except that the oxygen source gas is substituted with a nitrogen source gas. Accordingly, one of the reactant species preferably includes a metal-containing species with an organic or halide ligand, while a second reactant species includes a nitrogen-containing species. In the illustrated embodiment, the metal film comprises a titanium nitride (TiN) film formed by ALD in alternating, self-limiting metal and nitrogen phases separated by purge steps. In the example of Table VII, the exemplary metal source gas comprises titanium tetrachloride (TiCl.sub.4), the carrier gas comprises nitrogen (N.sub.2) and the nitrogen source gas preferably comprises ammonia (NH.sub.3).

Detailed Description Text - DETX (102):

In the next cycle, the first phase introduces TiCl.sub.4, which readily reacts with the surface of the titanium nitride monolayer, again leaving a chloride-terminated titanium layer. The second phase of the second cycle is then as described with respect to the first cycle. These cycles are repeated until a thickness of titanium nitride sufficient to perform a **barrier** function is formed. Preferably between about 5 nm and 50 nm, more preferably between about 10 nm and 30 nm of metal nitride is formed in this manner.

Detailed Description Text - DETX (104):

Table VIII above presents parameters for ALD of a conformal elemental metal layer over a capacitor dielectric. The process can be conducted immediately following formation of a **barrier** layer (see Table VII) or directly over the capacitor dielectric. The process is also similar to that of FIGS. 4A and 5, except that the oxygen source gas is substituted with a reducing agent. Accordingly, one of the reactant species preferably includes a metal-containing species with an organic or halide ligand, while a second reactant species includes a strong reducing agent. In the illustrated embodiment, the metal film comprises a tungsten (W) layer formed by ALD, in alternating metal and reducing phases separated by purge steps. In the example of Table VIII, the metal source gas comprises tungsten hexafluoride (WF.sub.6), the carrier gas comprises nitrogen gas (N.sub.2) and the reducing agent comprises triethyl boron ((CH.sub.3 CH.sub.2).sub.3 B) or TEB.

Detailed Description Text - DETX (105):

In the first phase of the first cycle, WF.sub.6 chemilsorbs upon the hydroxyl and oxygen bridge termination of the deposited high k dielectric, or upon the termination of a previously formed **barrier** layer. The metal source gas preferably comprises a sufficient percentage of the carrier flow, given the other process parameters, to saturate the dielectric surfaces. A monolayer of tungsten complex is left upon the dielectric, and this monolayer is self-terminated with halide tails.

Detailed Description Text - DETX (115):

Referring now to FIG. 8, wherein like reference numerals are used for like parts, a similar bottom electrode 300 is shown with a similarly conformal dielectric layer 302 over an HSG silicon layer 304. Additionally, a **barrier** layer 306 is formed between the dielectric 302 and the HSG silicon surface 304. In accordance with the example of Tables II and III above, for example, a thermally grown silicon nitride layer serves as the **barrier** layer 306 under a tantalum oxide dielectric 302. Thus, the readily oxidized HSG silicon 304 is somewhat protected against oxidation. Silicon nitride effectively becomes part of the capacitor dielectric, lowering the effective dielectric constant, but better protects the lower electrode 300 from oxidation.

Detailed Description Text - DETX (118):

In one example, where the capacitor dielectric comprises a volatile material such as Ta.sub.2 O.sub.5, the initial thin conductive film 308 comprises a thin (e.g., between about 10 nm and 30 nm) **barrier** layer, exemplified by the TiN formed by the process of Table VII. In this case, the remainder 310 of the top electrode preferably includes about another 100 nm of metal nitride to leave an effective thickness for the **barrier** function. The remaining portion 310 of the top electrode preferably also includes a more conductive material, such as an elemental metal, deposited thereover.